

PATENT SPECIFICATION

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(54) THERMOPLASTIC MOLDING COMPOSITIONS OF HIGH IMPACT STRENGTH

(71) We, BASF AKTIENGESSELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:-

5 The present invention relates to molding compositions based on a thermoplastically processable, partially crystalline plastics material, into which is mixed on elastomeric graft copolymer to improve the toughness. 5

10 It is known that thermoplastically processable, partially crystalline plastics materials, e.g. nylons, linear saturated polyesters, polyacetals, polyethers and others, are valuable materials for the manufacture of moldings and other shaped articles which are distinguished by excellent mechanical properties for numerous applications, for example by great rigidity, tensile strength and flexural strength, great surface hardness and good gloss. However, for various applications their impact strength is too low and drops rather rapidly below 20°C, because of the high glass transition temperature of these plastics. It is however desirable that the products should possess a good impact strength even at low ambient temperatures, and the other advantageous mechanical properties should not suffer, or should only do so to an acceptable degree. 15

20 Various proposals have been made for improving the impact strength of thermoplastically processable, partially crystalline plastics materials by admixture of elastomeric graft copolymers which have a glass transition temperature below -20°C. Inter alia, polyester molding compositions (German Laid-Open Application DOS 2,444,584), nylon molding compositions (German Laid-Open Application DOS 2,435,266) and polyoxymethylene molding compositions (German Laid-Open Application DOS 1,931,392 and DOS 1,964,156) modified with such elastomeric graft copolymers in order to improve their impact strength have been disclosed. According to these publications, the elastomeric graft copolymers to be employed for improving the impact strength are especially graft copolymers which contain styrene, acrylonitrile and/or an acrylic or methacrylic ester grafted onto a crosslinked, saturated polyacrylic ester rubber. It is true that such molding compositions have improved impact strength even at low temperatures, without substantial impairment of the other advantageous mechanical properties of the partially crystalline plastics material. However, the low temperature impact strength of these molding compositions is limited by the relatively high glass transition temperatures, in general not below about -40°C, of the crosslinked polyacrylate rubbers usually employed for the manufacture of the graft copolymers. It is true that if the thermoplastically processable, partially crystalline plastics materials are mixed with graft copolymers which contain a polybutadiene rubber (glass transition temperature about -80°C) as the grafting base, as described, for example, in German Laid-Open Application DOS 1,931,392, the low temperature impact strength of the molding compositions can be improved somewhat further because of the lower glass transition temperature of the polybutadiene rubber than that of the polyacrylate rubbers. However, because of the unsaturated nature of the rubber, the products exhibit unsatisfactory weathering resistance and aging resistance and their color is not stable; instead, they tend to discolor when exposed to heat or light. 30 35 40

45 Though the previously disclosed thermoplastic molding compositions based on polyesters, polyacetals, polyethers or nylons which have been modified to improve their impact strength each in themselves possess a number of good properties and numerous advantages, 45

it has not hitherto proved possible to provide compositions of high impact strength which are based on thermoplastically processable, partially crystalline plastics materials, exhibit a near-optimal combination of the desired mechanical properties and at the same time possess good weathering resistance and aging resistance, good low temperature impact strength, good surface characteristics, and a pure intrinsic color which is very stable, without substantial impairment of the original properties of the thermoplastically processable, partially crystalline plastics materials.

We have found that advantageous plastic molding compositions based on a thermoplastically processable, partially crystalline plastics material and having this optimum combination of mechanical properties may be obtained if the impact strength of the partially crystalline plastics material is modified by the use of an elastomeric graft copolymer which has been obtained by polymerizing a monomer or monomer mixture which gives a hard, glassy polymer compatible with the thermoplastically processable, partially crystalline plastics material, in the presence of an organopolysiloxane and/or of a silicone rubber.

Accordingly, the present invention provides a very tough thermoplastic molding composition which comprises

A. 100 parts by weight of a thermoplastically processable, partially crystalline plastics material,

B. from 1 to 50 parts by weight of an elastomeric graft copolymer in which the base rubber has a glass transition temperature of below -40°C and

C. from 0 to 100 parts by weight, based on 100 parts by weight of component A, of one or more reinforcing agents and/or fillers and/or additives, wherein component B is a graft copolymer which has been obtained by polymerizing

(i) from 10 to 50% by weight, based on component B, of a monomer or monomer mixture which forms a hard polymer, compatible with component A, in the presence of

(ii) from 90 to 50% by weight, based on component B, of a modified or unmodified organopolysiloxane and/or silicone rubber as the base rubber to be grafted.

The partially crystalline plastics material which is used as component A for the purposes of the invention, must be thermoplastically processable. This means that the processing temperature or plasticizing temperature of the plastics material should in general be less than 320°C and will preferably be in the range of from 150°C to 300°C . Because of the lower heat stability of the elastomeric graft copolymer to be admixed, higher processing temperatures can only be used under certain conditions.

Partially crystalline plastics materials, for the purposes of the present invention, are all plastics materials which have a degree of crystallinity in the range of from 5 to 95% and are either obtained directly in a partially crystalline form after processing, or can be obtained in such a form by a heat treatment. The crystallinity of the plastics materials may be determined in accordance with conventional methods, either from X-ray diagrams or by density measurements or by differential calorimetry. Preferred components A of the molding compositions according to the invention are nylons, polyesters, polyacetals, polyethers and polycarbonates.

Examples of suitable nylons are linear polycondensates of lactams of 6 to 12 carbon atoms and conventional polycondensates of diamines and dicarboxylic acids, e.g. nylon 6,6, nylon 6,8, nylon 6,9, nylon 6,10, nylon 6,12, nylon 8,8 and nylon 12,12. Further examples to be mentioned are nylon 6, nylon 11 and nylon 12, which are manufactured from the corresponding lactams. In addition, it is possible to use polycondensates of aromatic dicarboxylic acids, e.g. isophthalic acid or terephthalic acid, with diamines, e.g. hexamethylenediamine or octamethylenediamine, polycondensates of araliphatic starting materials, e.g. m- and p-xylylenediamines, with adipic acid, suberic acid and sebacic acid, and polycondensates based on alicyclic starting materials, e.g. cyclohexanedicarboxylic acid, cyclohexanediacetic acid, 4,4'-diaminodicyclohexylmethane and 4,4'-diaminodicyclohexylpropane. The nylons preferably have a relative viscosity of from 2.30 to 3.60, measured at 1% strength in concentrated sulfuric acid at 25°C .

The linear saturated polyesters which may be used as component A can be obtained either by polycondensation of a hydroxycarboxylic acid or, preferably, by synthesis from a dicarboxylic acid and a saturated diol. Polyesters of an aromatic dicarboxylic acid, especially terephthalic acid, with a saturated aliphatic diol, e.g. ethylene glycol or butane-1,4-diol, are preferred. The use of polybutylene terephthalate is particularly advantageous. It is also possible to employ modified polybutylene terephthalates which, in addition to terephthalic acid, contain other aromatic dicarboxylic acids or even aliphatic dicarboxylic acids, e.g. naphthalene-2,6-dicarboxylic acid or adipic acid, as base units. It is also possible to employ modified polybutylene terephthalates which, in addition to butane-1,4-diol, contain other aliphatic diols, for example neopentylglycol, ethylene glycol or hexane-1,6-diol. The polyesters should in general have a relative viscosity (measured in

an 0.5% strength solution in a 60:40 phenol/o-dichlorobenzene mixture at 25°C) of from 1.44 to 1.95, preferably from 1.50 to 1.75.

Examples of polyacetals which may be employed as component A are, in particular, the oxymethylene polymers, polyoxymethylene being of particular importance. However, oxymethylene copolymers which, in addition to oxymethylene groups, contain up to 30% by weight, preferably from 0.1 to 25% by weight, of other oxyalkylene groups, for example the oxyethylene group, the trimethylene oxide group or, preferably, the tetramethylene oxide group, are also suitable, as are terpolymers. The use of oxymethylene homopolymers in which the end groups of the molecules have been stabilized against degradation by esterifying, etherifying or some other conventional chain termination, is preferred. The oxymethylene polymers usually have a melting point above 130°C.

Polyethers which can be used as component A are, in the main, polyarylene ethers, amongst which polyphenylene oxides deserve particular mention. The use of poly-2,6-dimethyl-1,4-phenylene oxide is preferred, and in order to lower its melt viscosity and improve its processability, it may be advantageous to admix to it from 10 to 90% by weight of polystyrene (based on the mixture of polyphenylene oxide and polystyrene).

The preferred polycarbonate to use as component A in the molding compositions according to the invention is poly-2,2-propane-bis(4-phenyl)-carbonate, which is manufactured in accordance with conventional processes by reacting phosgene or diphenyl carbonate with 2,2-(diphenyl-4,4'-dihydroxy)-propane. Other preferred polycarbonates contain tetrachlorobisphenol A as an additional comonomer, which improves the fire resistance of the molding compositions.

An essential characteristic of the new molding compositions is that they contain component B, i.e. an elastomeric graft copolymer in which the elastomeric constituent is an organopolysiloxane and/or silicone rubber. The graft copolymers are obtained by polymerizing one or more monomers which form hard polymers, compatible with component A, in the presence of the organopolysiloxane and/or the silicone rubber, a substantial proportion of the monomers being grafted onto the organopolysiloxane and/or the silicone rubber. The manufacture of such graft copolymers has been disclosed in principles and is described, for example, in GB Patent Specification No. 1,401,086.

The graft copolymers used for the purposes of the invention are, in principle, all those of the above type, provided they possess elastomeric properties and provided the glass transition temperature of the organopolysiloxane and/or silicone rubber to be grafted is below -40°C, especially from -130 to below -40°C, preferably from -80°C to -130°C. The glass transition temperature can be determined by the methods described by B. Vollmert, Grundriß der makromolekularen Chemie, pages 406 - 410, Springer-Verlag, Heidelberg (1962).

The silicone rubbers which may be used are organopolysiloxanes which have already been cross-linked. The organopolysiloxanes and/or silicone rubbers are then grafted with the monomers which form hard polymers and are described in more detail below, i.e. these monomers are polymerized in the presence of the organopolysiloxane and/or silicone rubber. An example of a suitable organopolysiloxane for the manufacture of the graft copolymers is polydimethylsiloxane. Advantageous graft copolymers are obtained by starting from modified organopolysiloxanes and/or modified silicone rubbers, for example from those possessing vinyl and/or allyl side groups, as described, inter alia, in GB Patent Specification No. 1,401,086. The vinyl and/or allyl side groups facilitate the grafting of the monomers onto the organopolysiloxanes and/or the silicone rubber.

Particularly advantageous results are obtained by using, for the manufacture of the elastomeric graft copolymers (component B), organopolysiloxanes and/or silicone rubbers which contain groups which can be attacked by free radicals and are capable of hydrogen transfer or halogen transfer, and/or contain acrylyl and/or methacrylyl side groups, as described in German Laid-Open Patent Application DOS 2,539,572. Here, groups which can be attacked by free radicals and are capable of hydrogen transfer means groups which contain a reactive hydrogen which can be abstracted by free radicals. They include, above all, hydrogen bonded to a silicon atom, and also organic groups which contain reactive abstractable hydrogen, e.g. the p-ethylphenyl radical and the benzoyl radical. Similarly, groups which can be attacked by free radicals and are capable of halogen transfer means groups which contain a chlorine or bromine atom which can undergo a transfer reaction with free radicals. These include not only chlorine or bromine bonded to a silicon atom, but also alkyl, aralkyl and/or cycloalkyl groups containing chlorine or bromine bonded to an aliphatic or cycloaliphatic structure. The use of organopolysiloxanes and/or silicone rubbers which contain acrylyl and/or methacrylyl side groups as groups capable of undergoing grafting is particularly advantageous.

The organopolysiloxanes to be employed for the manufacture of the elastomeric graft copolymers in general have a molecular weight of from 20,000 to 1,000,000, preferably from

50,000 to 600,000 (weight-average molecular weight, determined in bromocyclohexane); if silicone rubbers are employed, they generally have a swelling ratio of from 5:1 to 40:1. Organopolysiloxanes and/or silicone rubbers possessing groups which can be attacked by free radicals and are capable of hydrogen transfer or halogen transfer, and/or possessing acrylyl and/or methacrylyl side groups, according to German Laid-Open Patent Application DOS 2,539,572, should preferably contain from 0.0001 to 0.6, more preferably from 0.0001 to 0.02, of the groups which can be attacked by free radicals and/or of the acrylyl and/or methacrylyl groups, per structural unit of the organopolysiloxane or of the silicone rubber. This means that one group which can be attacked by free radicals and/or one acrylyl and/or methacrylyl side group is present for about from 2 to 10,000, preferably from 50 to 10,000, silicon atoms of the organopolysiloxane or of the silicone rubber. It is particularly advantageous to have from 0.001 to 0.02 of the groups which can be attacked by free radicals and/or of the acrylyl and/or methacrylyl side groups per structural unit of the rubber component. The manufacture of the organopolysiloxanes or of the silicone rubber which can be used, in turn, to manufacture the graft copolymers to be employed according to the invention, has been disclosed per se, and can be carried out in accordance with the conventional methods.

Of course, silicone copolymers can also be used as the grafting base for the manufacture of the elastomeric graft copolymers. The groups which can be attacked by free radicals and are capable of hydrogen transfer or halogen transfer, and/or the acrylyl and/or methacrylyl groups, are essential for subsequent grafting of the organopolysiloxanes and/or silicone rubbers. These groups serve - to different degrees depending on their reactivity - as grafting points, at which the polymer molecule subsequently continues to grow.

To manufacture the elastomeric graft copolymers, the organopolysiloxane and/or silicone rubber is grafted with the monomer(s) which form hard polymers compatible with component A. For this purpose, the monomer(s) which form hard polymers which are compatible with component A may be polymerized in the presence of the organopolysiloxane and/or silicone rubber in a conventional manner customary for the manufacture of polymers which have been modified to improve their impact strength. Suitable monomers or monomer mixtures for grafting the organopolysiloxanes and/or silicone rubbers are all those which are capable of forming hard, glassy polymers which are compatible with the thermoplastically processable, partially crystalline plastics (component A). As a first approximation, the solubility parameter δ of the polymers can be employed as a measure of the compatibility. The solubility parameter δ of polymers is defined as described by J.H. Hildebrand and R.L. Scott, *The Solubility of Nonelectrolytes*, 3rd edition (1950), Reinhold Publishers, New York. It can be determined by the method of K.L. Hoy, *Journal of Paint Technology*, 42 (1970), 76, from the group increments and bond increments of the polymers. Accordingly, the monomers or monomer mixtures for grafting the organopolysiloxanes and/or silicone rubbers should in general be selected so that the polymers manufactured therefrom should have the same, or virtually the same, solubility parameter as the thermoplastically processable, partially crystalline plastics (component A) which are to be modified. A further condition to be met is that the monomers used for grafting the organopolysiloxanes and/or silicone rubbers should form polymers which possess sufficient heat stability at the processing temperatures of the partially crystalline plastics (component A).

Suitable monomers for the grafting of the organopolysiloxanes and/or silicone rubbers are, in particular, styrenes; the side-chain-substituted styrenes, e.g. α -methylstyrene; the nuclear-alkylated styrenes, e.g. vinyltoluene; alkyl acrylates derived from alcohols of 1 to 8 carbon atoms, e.g. ethyl acrylate, propyl acrylate or n-butyl acrylate; alkyl methacrylates derived from alcohols of 1 to 4 carbon atoms, e.g. methyl methacrylate and ethyl methacrylate; acrylonitrile and methacrylonitrile; and mixtures of these monomers. Advantageously, the graft copolymers have a substantial content of polar groups. For this reason, it is advantageous to employ, for the grafting reaction, monomers or monomer mixtures which contain more than 10% by weight, based on the monomers to be grafted, of acrylic esters and/or methacrylic esters and/or acrylonitrile and/or methacrylonitrile.

Preferably, monomer mixtures of styrene and acrylonitrile are employed, with the acrylonitrile content of these mixtures depending on the desired and required solubility parameter δ and being, in general, from 10 to 70% by weight, based on the monomer mixture. In these mixtures, the styrene can also be replaced entirely or partially by α -methylstyrene, ethyl acrylate, propyl acrylate, n-butyl acrylate and/or ethyl methacrylate. Similarly, the acrylonitrile can be entirely or partially replaced by methacrylonitrile. Such monomer mixtures may be used, depending on their composition, for the manufacture of, for example, elastomeric graft copolymers which are to be employed for modifying nylons, polyesters, polycarbonates or polyethers. If, for example, polybutylene terephthalate or polyethylene terephthalate is employed as component A in the mixtures according to the

invention, methyl methacrylate alone can also be used for grafting the organopolysiloxanes and/or silicone rubbers. The use of methacrylonitrile as the sole grafting monomer is advisable, for example, when polyoxymethylene is used as component A.

5 The elastomeric graft copolymers are manufactured by polymerizing from 10 to 50% by weight of the monomer or monomer mixture in the presence of from 90 to 50% by weight of the organopolysiloxane and/or silicone rubber. Preferably, degrees of grafting of from 30 to 40% by weight, based on the elastomeric graft copolymer, are employed when manufacturing the said copolymer. The graft polymerization may be carried out, as mentioned above, in a conventional manner for the manufacture of elastomeric graft copolymers, as a mass polymerization, solution polymerization or aqueous dispersion polymerization. Combined polymerization processes, in which an initial mass polymerization or solution polymerization is followed by completing the polymerization in aqueous dispersion can also be used. The conventional polymerization assistants, e.g. free radical initiators, regulators, dispersants and the like, may be used for the graft polymerization. 10 Preferably, the polymerization of the monomer or monomer mixtures in the presence of the organopolysiloxanes and/or silicone rubbers is carried out by a straightforward suspension or emulsion polymerization process, as has been disclosed and described for the manufacture of ABS or ASA polymers. In such a process, a mixture of the monomers with the organopolysiloxane and/or the silicone rubber, which should be present in a very finely divided form, is dispersed in water in the presence of the conventional emulsifiers or suspending agents and is then polymerized at from 30 to 100°C, preferably from 40 to 80°C. 15 For polymerization in aqueous emulsion, water-soluble initiators, e.g. organic water-soluble peroxides, percarbonates, persulfates, perborates or redox catalysts, are used. For polymerization in aqueous suspension, it is advantageous to employ monomer-soluble organic peroxides, e.g. benzoyl peroxide, dicumyl peroxide or di-tert.-butyl peroxide, or azodiisobutyronitrile. Examples of emulsifiers are alkyl sulfonates, alkyl sulfates, aralkyl sulfonates and aralkyl sulfates, and the salts of fatty acids; these are used in concentrations of from 0.1 to 5% by weight. Suitable suspending agents are the conventional protective colloids, e.g. methylcellulose, hydroxypropylcellulose, polyvinyl alcohol and polyvinylpyrrolidone. Preferably, the elastomeric graft copolymers are manufactured in aqueous emulsion, as described, for example, in German Patents 1,260,135 and 1,238,207 for the manufacture of ABS polymers or ASA polymers. 20

The elastomeric graft copolymers are admixed to the thermoplastically processable, partially crystalline plastics materials in such amounts that the new molding compositions contain from 1 to 50 parts by weight, advantageously from 5 to 20 parts by weight, of components B per 100 parts by weight of component A. A weight ratio of component A to component B of 9 : 1 is particularly advantageous. The use of more than 50 parts by weight of the elastomeric graft copolymer per 100 parts by weight of the thermoplastically processable, partially crystalline plastics material is excluded as it is not of advantage; it is true that it further increases the impact strength of the molding compositions, but the E-modulus and yield stress then become so low as not to suffice for many applications. 25

Where polyesters, e.g. polyethylene terephthalate or polybutylene terephthalate, are employed as component A it can furthermore be useful, for certain purposes, to add nucleating agents in order to accelerate the crystallization of the polyesters on processing. 30 Nucleating agents which may be added are the conventional materials, e.g. calcium carbonate, aluminum silicate or talc. The nucleating agent may be added at various stages of the process of manufacture of the molding compositions. For example, it may be added during manufacture of the polyester, or may be added, together with the elastomeric graft copolymer and with or without additives, to the finished polyester. 35

The elastomeric graft copolymers which have been described may also be added in order to increase the impact strength of molding compositions based on filled and/or reinforced thermoplastically processable, partially crystalline plastics. Accordingly, the molding compositions of the invention may contain, in addition to components A and B, from 0 to 100 parts by weight, per 100 parts by weight of component A, of conventional reinforcing agents or fillers or additives or mixtures of these. 40

Suitable reinforcing fillers are those which increase the rigidity of the thermoplastically processable, partially crystalline plastics. Preferred fillers are fibrous materials, especially glass fibers of low-alkali E-glass having a fiber diameter of from 8 to 14 µm and a glass fiber length, in the finished injection molding, of from 0.01 to 0.5 mm. The glass fibers may be employed as continuous filaments or as chopped or milled glass fibers and can be provided with a suitable sizing system and an adhesion promoter or adhesion promoter system, based on a silane. 45

However, other fibrous reinforcing materials, e.g. carbon fibers, K titanate single-crystal fibers, gypsum fibers, aluminum oxide fibers or asbestos fibers, may also be incorporated. 50 Non-fibrous fillers, e.g. glass beads, hollow beads, chalk, quartz, natural or calcined 55

kaolins, can also be used, as can combinations of these materials with glass fibers. These fillers, like the glass fibers, can be provided with a size and/or an adhesion promoter or adhesion promoter system. In addition to, or in place of, the reinforcing agents, the molding compositions according to the invention may contain other fillers, e.g. metal
5 powders, carbon powder, preferably graphite powder with a particle size of from 0.1 to 100 μm , and mineral fillers, e.g. talc or barium sulfate. 5

Furthermore, fire-retardant additives based on elementary red phosphorus, phosphorus compounds, halogen compounds, nitrogen compounds, antimony oxides, iron oxides and zinc oxide, as well as dyes and colored pigments, heat stabilizers, thermooxidative
10 stabilizers and UV stabilizers, waxes, lubricants and processing assistants, which ensure 10 trouble-free extrusion an injection molding, and antistatic agents, may be added to the molding compositions according to the invention. In these cases, again, the impact strength of the partially crystalline plastics, which as a rule is greatly reduced by the admixture of the above additives, can be greatly improved, and brought back to near its starting level, by the
15 admixture, according to the invention, of the elastomeric graft copolymers which have been 15 described.

Conventional processes for mixing thermoplastic polymers can be used for the manufacture of molding compositions within the invention. For example, the compositions can be manufactured by using any suitable mixing equipment, e.g. mills, calenders,
20 kneaders or extruders. The mixing temperatures are advantageously above the crystallite 20 melting point of the partially crystalline plastics and are in general from 150 to 320°C, preferably from 170 to 300°C. The polymers are fused and thoroughly mixed, with or without the other additives described. However, because of the good compatibility of components A and B it is possible to process a pulverulent mixture of the components
25 directly by means of an injection molding machine, without a preliminary fusion process. 25 In such a case, the screw of the injection molding machine itself achieves homogeneous mixing.

The molding compositions according to the invention, based on the thermoplastically processable, partially crystalline plastics, should have a very low moisture content,
30 preferably of less than 0.02% by weight. 30

The addition of the elastomeric graft copolymers, described above, does not adversely influence the processing stability of the thermoplastically processable, partially crystalline plastics materials. The processing of the new molding compositions by extrusion or
35 injection molding is preferably carried out at from 170 to 300°C, with the mold, in the latter 35 case, being at from 50 to 150°C.

Molding compositions within the invention are above all distinguished by their combination of good mechanical properties. In addition to good weathering resistance and aging resistance they have a good low temperature impact strength, whilst the original
40 mechanical properties of the thermoplastically processable partially crystalline plastics 40 material, e.g. tensile strength, resistance to elongation or modulus of elasticity, are only impaired slightly, if at all. Furthermore, the molding compositions have a very stable color and exhibit a very pure intrinsic color in the unpigmented state. The molding compositions give partially crystalline, dimensionally stable moldings which have a low moisture
45 absorption, high resistance to solvents and good surface quality. The molding compositions 45 can be processed by the conventional methods for thermoplastics materials, e.g. extrusion and injection molding, to give housings, containers, shells, gearwheels, machinery components, bobbins, slide components, pipes, rods, hoses and the like.

The Examples which follow illustrate the invention. In the Examples, parts and percentages are by weight, unless stated otherwise.

The elastomeric graft copolymers (component B) employed in the Examples were
50 obtained by aqueous emulsion polymerization of the monomers or monomer mixtures, 50 specified in the Examples, in the presence of a polydimethylsiloxane which contains acrylyl side groups and has a weight-average molecular weight of about 560,000 and a glass transition temperature of -120°C. The graft copolymers thus produced were mixed with
55 various thermoplastically processable, partially crystalline plastics materials (component A) 55 at the mixing temperatures stated in the Examples, in a twin-screw extruder, using a weight ratio of partially crystalline plastics material (component A) to graft copolymer (component B) of 9 : 1, and the mixture was then granulated. These granules were dried to a moisture content of less than 0.02%. They were then converted by means of an injection molding
60 machine, at the stated material temperatures and mold temperatures, to give standard small 60 bars and molded dumbbell-shaped bars. The former were used to determine the notched impact strength of the products in accordance with DIN 53,453 and the latter to determine the E-modulus of the molding compositions in accordance with DIN 53,457.

Example 1

Component A: nylon 6, having a relative viscosity of 2.57 (measured in 1% strength solution in 98% strength sulfuric acid at 25°C).

5 Component B: a graft copolymer of 100 parts of the organopolysiloxane and 60 parts of a monomer mixture of 50% of styrene and 50% of acrylonitrile. 5

Mixing temperature of A with B: 240°C.

Injection molding conditions for the manufacture of the test specimens: material temperature 250°C, mold temperature 60°C.

10 **Example 2**

Component A: nylon 6,6, having a relative viscosity of 2.50 (measured in 1% strength solution in 98% strength sulfuric acid at 25°C). 10

Component B: a graft copolymer of 100 parts of the organopolysiloxane and 50 parts of a monomer mixture of 40% of styrene and 60% of acrylonitrile.

15 Mixing temperature of A with B: 270°C. 15

Injection molding conditions for the manufacture of the test bars: material temperature 290°C, mold temperature 60°C.

20 **Example 3**

Component A: polyoxymethylene having a melt index of 13 g/10 minutes, measured according to DIN 53,736 (190°C/2.16 kg). 20

Component B: a graft copolymer of 100 parts of the organopolysiloxane and 50 parts of a monomer mixture of 70% of styrene and 30% of acrylonitrile.

25 Mixing temperature of A with B: 190°C.

Injection molding conditions for the manufacture of the test specimens: material temperature 200°C, mold temperature 60°C. 25

Example 4

Component A: polyethylene terephthalate having a relative viscosity of 1.55 (measured in an 0.5% strength solution in a 60:40 phenol/o-dichlorobenzene mixture at 25°C). 30

Component B: a graft copolymer of 100 parts of the organopolysiloxane and 70 parts of a monomer mixture of 75% of styrene and 25% of acrylonitrile.

Mixing temperature of A with B: 280°C.

35 Injection molding conditions for the manufacture of the test specimens: material temperature 300°C, mold temperature 140°C. 35

Example 5

Component A: polybutylene terephthalate having a relative viscosity of 1.63 (measured in an 0.5% strength solution in a 60:40 phenol/o-dichlorobenzene mixture at 25°C).

40 Component B: a graft copolymer of 100 parts of the organopolysiloxane and 70 parts of a monomer mixture of 75% of styrene and 25% of acrylonitrile. 40

Mixing temperature of A with B: 240°C.

Injection molding conditions for the manufacture of the test specimens: material temperature 255°C, mold temperature 60°C.

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Example 6

Component A: polycarbonate based on 2,2-(diphenyl-4,4'-dihydroxy)-propane and having a relative viscosity of 1.33 (measured in an 0.5% strength solution in a 60:40 phenol/o-dichlorobenzene mixture at 25°C).

50 Component B: a graft copolymer of 100 parts of the organopolysiloxane and 60 parts of a monomer mixture of 75% of styrene and 25% of acrylonitrile. 50

Mixing temperature of A with B: 280°C.

Injection molding conditions for the manufacture of the test specimens: material temperature 290°C, mold temperature 60°C.

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Example 7

Component A: a mixture of poly-2,6-dimethyl-1,4-phenylene oxide with polystyrene (Noryl 731 from General Electric, "Noryl" is a Registered Trade Mark).

60 Component B: a graft copolymer of 100 parts of the organopolysiloxane and 50 parts of styrene. 60

Mixing temperature of A and B: 270°C.

Injection molding conditions for the manufacture of the test specimens: material temperature 280°C, mold temperature 110°C.

65 The measurements obtained on injection moldings produced in accordance with the Examples are summarized in the Table which follows. As may be seen from these values, 65

the addition, according to the invention, of the elastomeric graft copolymers based on organopolysiloxanes and/or silicone rubbers to the thermoplastically processable, partially crystalline plastics increases their notched impact strength by about a factor of 3 compared to the unmodified partially crystalline plastics, whilst at the same time the modulus of elasticity of the products only drops by about 10%.

Similar results are also obtained by employing, in the Examples, elastomeric graft copolymers in which the styrene has been entirely or partially replaced by α -methylstyrene, ethyl acrylate, n-butyl acrylate and/or ethyl methacrylate.

TABLE

Ex- ample	Notched impact strength of pure component A kJ/m ² at				Notched impact strength of mixture A + B kJ/m ² at			E-modulus of pure component A N/mm ² at		E-modulus of mixture A + B N/mm ² at	
	23°C	-20°C	-40°C	-60°C	23°C	-20°C	-40°C	-60°C	23°C	23°C	23°C
1 ⁺	5.1	2.9	2.3	1.4	15.6	11.3	9.2	7.3	2,500	2,270	2,270
2 ⁺	2.8	1.6	1.2	0.7	8.3	5.2	4.2	3.8	2,900	2,630	2,630
3	5.0	4.5	4.0	3.1	19.3	17.3	16.8	15.2	3,100	2,720	2,720
4	3.2	2.3	1.8	1.1	10.0	8.0	7.5	6.3	3,100	2,830	2,830
5	4.5	3.0	2.1	1.5	11.8	9.9	9.1	7.8	2,650	2,450	2,450
6	25.0	16.8	10.0	6.4	56.2	48.7	41.2	35.2	2,080	1,850	1,850
7	2.2	1.4	0.7	0.5	5.7	4.5	4.0	2.7	2,450	2,310	2,310

⁺ measured on the dry material

WHAT WE CLAIM IS:-

1. A very tough thermoplastic molding composition which comprises.
 - A) 100 parts by weight of a thermoplastically processable, partially crystalline plastics material, and
 - 5 B) from 1 to 50 parts by weight of an elastomeric graft copolymer prepared from a rubber grafting base which has a glass transition temperature of below -40°C , wherein the graft copolymer B has been obtained by polymerizing
 - (i) from 10 to 50% by weight, based on component B, of a monomer or monomer mixture which forms a hard polymer, compatible with component A, in the presence of
 - 10 (ii) from 90 to 50% by weight, based on component B, of a modified or unmodified organopolysiloxane or silicone rubber or a mixture of these as the rubber grafting base.
 2. A thermoplastic molding composition as claimed in claim 1, wherein an organopolysiloxane or silicone rubber which contains vinyl or allyl groups at least as side groups, is used for the manufacture of component B.
 - 15 3. A thermoplastic molding composition as claimed in claim 1, wherein an organopolysiloxane or silicone rubber which contains groups which can be attacked by free radicals and are capable of hydrogen or halogen transfer, acrylyl groups and/or methacrylyl groups, at least as side groups, is used for the manufacture of component B.
 4. A thermoplastic molding composition as claimed in any of claims 1 to 3, which
 - 20 contains from 5 to 20 parts by weight of components B per 100 parts by weight of component A.
 5. A thermoplastic molding composition as claimed in any of claims 1 to 4 which additionally contains
 - 25 C) up to 100 parts by weight, based on 100 parts by weight of component A, of at least one reinforcing agent, filler and/or additive.
 6. A thermoplastic molding composition as claimed in any of claims 1 to 5, wherein component A is a nylon having a relative viscosity of from 2.30 to 3.60, a linear saturated polyester having a relative viscosity of from 1.44 to 1.95, an oxymethylene polymer having a melting point above 130°C , a polyarylene ether or a polycarbonate.
 - 30 7. A thermoplastic molding composition as claimed in any of claims 1 to 6, wherein component A has a processing temperature of from 150 to 300°C .
 8. A thermoplastic molding composition as claimed in any of claims 1 to 7, wherein the glass transition temperature of the rubber grafting base of component B is from -80 to -130°C .
 - 35 9. A thermoplastic molding composition as claimed in any of claims 1 to 8, wherein the organopolysiloxane or silicone rubber is based on dimethyl siloxane.
 10. A thermoplastic molding composition as claimed in any of claims 1 to 9, wherein component B is based on an organopolysiloxane having a weight-average molecular weight of from 50,000 to 600,000.
 - 40 11. A thermoplastic molding composition as claimed in any of claims 1 to 10, wherein component B is based on a silicone rubber having a swelling ratio of from 5:1 to 40:1.
 12. A thermoplastic molding composition as claimed in any of claims 1 to 11, wherein the monomers i) for component B include more than 10% by weight of an acrylic or methacrylic ester, acrylonitrile and/or methacrylonitrile.
 - 45 13. A thermoplastic molding composition as claimed in any of claims 1 to 12, wherein component B has been manufactured by aqueous emulsion polymerization of the monomers i) on the rubber grafting base ii).
 14. A thermoplastic molding composition substantially as described in any of the foregoing Examples.
 - 50 15. Moldings made from thermoplastic molding compositions as claimed in any of claims 1 to 14.

16. A method of making a toughened thermoplastic molding composition as claimed in claim 1 which includes preparing an elastomeric graft copolymer by polymerising

(i) from 10 to 50% by weight, based on the graft copolymer, of a monomer or monomer mixture which forms a hard polymer, compatible with component A, in the presence of

5 (ii) from 90 to 50% by weight, based on the graft copolymer, of a modified or unmodified organopolysilocane or silicone rubber or a mixture of these as a rubber grafting base having a glass transition temperature of below -40°C , and admixing the elastomeric graft copolymer in an amount of from 1 to 50 parts by weight with 100 parts by weight of component A which is a thermoplastically processable, partially crystalline plastics material.

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